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DEVELOPMENT OF A COMPREHENSIVE AND PREDICTIVE REACTION MECHANISM OF LIQUID HYDROCARBON FUEL COMBUSTION

(Grant/Contract Number FA9550-05-1-0010)

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SUMMARY/OVERVIEW:

Studies were conducted in several relevant areas, including (1) a gas-kinetic analysis for the transport properties of long chain molecules in dilute gases, (2) quantum-chemistry, master equation modeling of the unimolecular decomposition of *ortho*-benzyne, (3) extension of the previously developed H₂/CO model to combustion pressure as high as 600 atm, and (4) a methodology for kinetic uncertainty propagation currently under development. These projects represent the two key ingredients that are necessary for the success of the overall research program: (a) an accurate physico-chemical property database for combustion kinetics, and (b) a unified and optimized kinetic model for liquid aliphatic and aromatic fuel combustion with quantifiable uncertainties.

TECHNICAL DISCUSSION:

1. Transport Theory of Long Chain Molecules in Dilute Gases

One of the major theoretical hurdles to obtain a quantitative understanding of the combustion chemistry of jet fuels and their surrogates is the lack of a suitable theory to describe the diffusion coefficient of long chain aliphatic molecules. Although the Chapman-Enskog theory is traditionally employed to calculate the binary diffusion coefficient, its underlying assumption of spherical potentials for the collision pair renders the applicability of the theory questionable. In this work, a rigorous, gas-kinetic theory analysis was carried out, and analytical equations are developed for the diffusion coefficient of long-chain molecules in the limits of specular and diffuse scattering.

A long-chain molecule may be approximated as a straight and rigid cylinder. Consider a cylinder with length equal to L and diameter D . Gas-kinetic theory analysis shows that the instantaneous drag force due to relative motion of a cylinder in a dilute gas may be given by

$$F_{s/d} = \frac{1}{2} \sqrt{(1 + 5 \sin^2 \alpha / 4) 2\pi m_r k T N L D V} \Omega_{s/d}^{(1,1)*} \quad (1)$$

where the subscript “ s/d ” denotes specular or diffuse scattering, α is the angle of the cylinder relative to the flow, m_r is the reduced mass, k is the Boltzmann constant, T is the temperature, N is the gas number density, V is the relative velocity. In eq. (1) $\Omega_{s/d}^{(1,1)*}$ is the reduced collision integral given by

$$\Omega_{s/d}^{(1,1)*} = \frac{\int_0^\infty \gamma^5 \exp(-\gamma^2) \mathcal{Q}_{s/d}(g) d\gamma}{LD} \quad (2)$$

where $\mathcal{Q}_{s/d}(g)$ is the collision cross section, defined in the two limiting scattering scenario as

$$\mathcal{Q}_s(g) = L \int_{-\infty}^{\infty} (1 - \cos \chi) db, \quad (3a)$$

and

$$\mathcal{Q}_d(g) = L \left[\int_{-b_0}^{b_0} \left(1 + \frac{1}{g} \sqrt{\frac{\pi kT}{2m_r}} \sin \frac{\chi}{2} \right) db + \int_{b_0}^{\infty} (1 - \cos \chi) db + \int_{-\infty}^{-b_0} (1 - \cos \chi) db \right], \quad (3b)$$

respectively. In eqs (3), the angle χ is given by

$$\chi(g, b) = \pi - 2b \int_{r_m}^{\infty} \frac{dr}{\sqrt{1 - \frac{b^2}{r^2} - \frac{\Phi(r, L)}{m_r g^2 / 2}}} \quad (4)$$

where r is the center-to-axial distance between the gas molecule and cylinder, r_m is the distance of the closest encounter, and $\Phi(r, L)$ is the potential function between the gas molecules and cylinder. In the limit of rigid-body collision, it may be shown that

$$\Omega_s^{(1,1)*} = 4/3 \quad (5a)$$

and

$$\Omega_d^{(1,1)*} = 1 + 3\pi^2/64. \quad (5b)$$

Realistically molecular scattering always lies between the two limiting scattering models. Similar to the treatment of nanoparticle transport, a parameter may be introduced here to give a mixed scattering model, such that an average, reduced collision integral may be defined as

$$\Omega_{avg}^{(1,1)*} = \varphi \Omega_s^{(1,1)*} + (1 - \varphi) \Omega_d^{(1,1)*}, \quad (6)$$

where φ is termed as the momentum accommodation function, which ranges from 0 to 1. From the knowledge of gas-nanoparticle scattering, it may be speculated that for long-chain aliphatic molecules φ is close to unity.

The instantaneous binary diffusion coefficient of a cylinder in a dilute gas may be obtained from the Stokes-Einstein relation, through the drag coefficient, as

$$D_{12} = 2 \sqrt{\frac{kT}{(1 + 5 \sin^2 \alpha/4) 2\pi m_r}} \frac{1}{NLD \Omega_{avg}^{(1,1)*}}. \quad (7)$$

An angle-averaged diffusion coefficient is obtained by replacing α by the mean angle $\bar{\alpha}$ of the orientation of the cylinder with respect to its diffusion direction.

The remaining work will be (a) to examine the potential function $\Phi(r,L)$ and to determine a suitable, parameterized form for this function, and (b) to carry out suitable experiments to determine the diffusion coefficients of representative, long-chain aliphatic molecules. Both components of the study are required to validate the theory developed.

2. Kinetics of unimolecular decomposition of *ortho*-benzyne

The kinetics of *ortho*-benzyne is an integral part of aromatics oxidation at high temperatures. Previously, it was concluded that the dominant channel of *ortho*-benzyne decomposition is through the concerted unimolecular dissociation leading to diacetylene and acetylene,



Recent shock-tube studies at DLR suggest that an additional reaction channel may become active at temperatures > 1600 K. This channel is characterized by the production of the H atom,



The shock tube study used 1,2-diiodobenzene is the precursor for *ortho*-benzyne.

In this study, we examined the potential energy surface of *ortho*-benzyne decomposition by molecular orbital calculations. The computation was carried out at the CCSD(T)/6-31G(d)//B3LYP/6-31G(d) level of theory. The minimum energy barrier for H production was computed to be 106 kcal/mol from *ortho*-benzyne. This energy barrier renders direct H production implausible below 2000 K. Subsequently, the reaction rate coefficient was analyzed by master equation modeling. Kinetic modeling shows that below 2000 K the apparent production of the H atom is due to the decomposition of the precursor compound, rather than the decomposition of *ortho*-benzyne.

3. H₂/CO combustion up to 600 atm

This is a collaborative research project with Professor Brezinsky at UIC. In this study, the high pressure oxidation of dilute CO mixtures doped with 150-200 ppm of H₂ has been studied behind reflected shock waves in the UIC high pressure single pulse shock tube. The experiments were performed over the temperature range from 1000-1500 K and pressures spanning 21-500 bars for stoichiometric ($\Phi=1$) and fuel lean ($\Phi=0.5$) oxidation. Stable species sampled from the shock tube were analyzed by standard GC, GC/MS techniques. The experimental data obtained were simulated using a previously published detailed model for H₂/CO combustion. Simulations showed that within experimental error the kinetic model was able to capture the experimental trends for the lower pressure data sets (average nominal pressures of 24 and 43 bars). However the model under predicts the CO and O₂ decay and subsequent CO₂ formation for the higher pressure data sets (average nominal pressures of 256 and 450 bars). The current elevated pressure data sets span a previously unmapped regime and have served to probe HO₂ radical reactions which appear to be among the most sensitive reactions in the model under these conditions. With updated rate parameters for

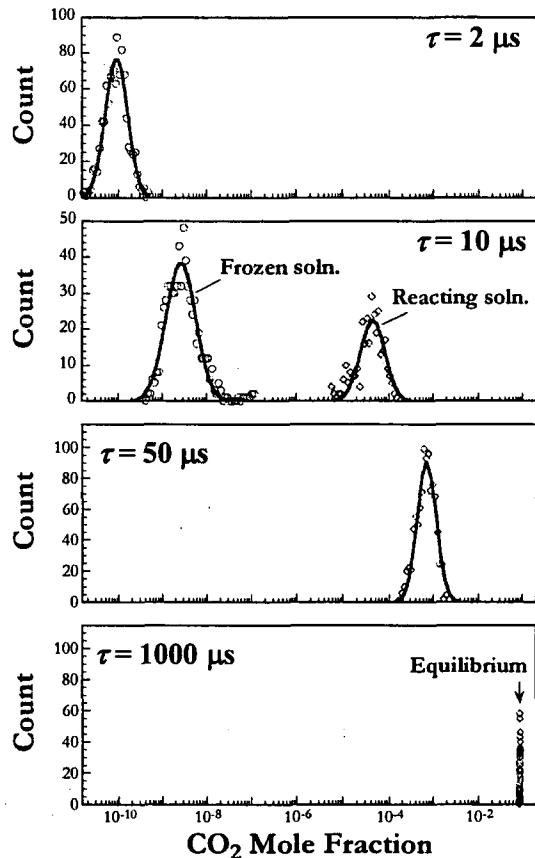
$\text{HO}_2 + \text{OH} = \text{O}_2 + \text{H}_2\text{O}$ the model is able to reconcile the elevated pressure data sets thereby extending the capability of the reaction model to an extreme range of conditions.

This work is reported in ref. [1].

4. Methodology of kinetic uncertainty propagation

We begin to develop a mathematical procedure to propagate kinetic uncertainty into combusting flow simulations. Figure 1 shows the statistical distributions of CO_2 mass fraction of ethylene oxidation in air in a perfectly stirred reactor ($\phi = 1.0$, $T = 1400$ K and $p = 1$ atm) as a function of the residence time τ . These distributions were obtained by Monte Carlo simulations. Although they nicely predict the wide distributions under the conditions where the residence time is limited, and the bifurcation of the distribution near the turning points, Monte Carlo simulations are inherently expansive. Currently, we are looking at a suitable mathematical procedure by which these distribution functions can be computed directly.

Figure 1. Statistical distributions of PSR solutions for the CO_2 mass fraction (C_2H_4 -air mixture, $\phi = 1.0$, $T = 1400$ K and $p = 1$ atm).



AFOSR SPONSORED PUBLICATIONS AND PRESENTATIONS:

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6. Chen, X., You, X., Braun-Unkhoff, B., Naumann, C., Frank, P., Just, T., and Wang, H. "Shock tube pyrolysis of 1,2-diiodobenzene—kinetics of H atom production in high-temperature thermal decomposition of *ortho*-benzyne." poster paper presented at the *6th International Conference of Chemical Kinetics*, National Institute of Standards and Technology, Gaithersburg, Maryland, July 25-29, 2005.